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(S7) Abstract: Acrylate, or methacrylate, or allylic, functionalized polyfluorooxetanes are disclosed for use in radiation curable coating compositions. These acrylate, or methacrylate, or allylic, functionalized polymers provide improvements in wetting and surface properties that have previously been provided by migratory chemicals such as waxes and oils. The partially or fully fluorinated side groups of the fluorooxetanes are believed to be disproportionately present at the interfaces between the coating and the substrate and between the coating and the atmosphere.

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RADIATION CURABLE COATING CONTAINING POLYFLUOROOXETANE**CROSS REFERENCE**

This is a U.S. patent application of U.S. provisional application 60/141,532, filed June 28, 1999 for a Radiation Curable Coating Containing Polyfluorooxetane, which is hereby fully incorporated by reference.

FIELD OF INVENTION

Radiation curable coatings are typically formulated using unsaturated monomers and oligomers or polymers with unsaturated or reactive groups such as oxiranes therein that can be polymerized upon exposure to electron beams or exposure to ultraviolet radiation when photoinitiators are present. Polyfluorooxetane refers to oligomers and polymers that contain fluorine containing groups pendant from the oxetane backbone. The fluorine containing groups contribute low surface tension to the coating and some stain release properties.

BACKGROUND OF THE INVENTION

Traditionally radiation curable coatings utilized combinations of silicone oils, wetting agents and polyethylene waxes to provide smoothness, abrasion resistance, low friction and scratch resistance. However these materials can be largely fugitive (unreacted) in nature and thus migratory, leading to handling problems, lower durability and can work at cross-purposes leading to decreases in other coating properties such as gloss.

U.S. Patent 5,411,996 disclosed the use of fluoroalcohol in U.V. epoxy-silicone coating formulations. The fluorinated alcohols were used to solubilize the U.V. initiator (sulfonium salt) to allow the polymerization reaction to occur.

U.S. Patent 5,081,165 related to an anti-fouling coating composition comprising a photopolymerization initiator or thermal polymerization initiator and fluorine containing (meth)acrylate.

U.S. Patent 4,833,207 relates to a curable composition for forming a cladding for an optical fiber having a refractive index of about 1.43 to 1.60.

U.S. Patent 5,674,951 discloses isocyanate functionalized polyoxetane polymers with pendant fluorinated side chains that can optionally be chain extended with polyoxetanes or other polyethers, have the isocyanate group blocked, and be crosslinked into a network. These coatings were effective for glass run channels.

SUMMARY OF THE INVENTION

Polyfluorooxetane oligomers and polymers can be functionalized with acrylate, or methacrylate, or allylic, end groups and thereafter used as a polyacrylate in a radiation curable coating composition. These polyfluorooxetanes could also be called fluorinated polyoxetanes or polyoxetanes with partially fluorinated pendant side groups (chains). These fluorinated oxetane repeating units have a single pendant fluorinated side group per repeating unit or they can have two pendant fluorinated side groups per repeating unit. The coating composition comprises the traditional components to a radiation curable coating which include the acrylate, or methacrylate, or allylic, terminated oligomers or polymers, monomer, optional UV initiator, optional second polyfunctional acrylate, or methacrylate, or allylic, oligomer or polymer, and optionally other additives like pigments, plasticizers, rheology modifiers etc.

The acrylate, or methacrylate, or allylic, functionalized polyfluorooxetane can be produced by several methods, but due to the lower reactivity of the hydroxyl groups of the polyfluorooxetane with isocyanate and epoxy groups, it is desirable to sequentially add the reactants so nearly complete functionalization of the polyfluorooxetane can be achieved. Typically an isocyanate or epoxy functionalize polyfluorooxetane is first formed and that is reacted with a hydroxy alkyl acrylate, or methacrylate, or allylic, to form the acrylate, or methacrylate, or allylic, terminated polyfluorooxetane. Alternatively the acrylate, or methacrylate,

or allylic, can be epoxy or isocyanate functionalized and that compound reacted with the polyfluorooxetane.

DETAILED DESCRIPTION OF THE INVENTION

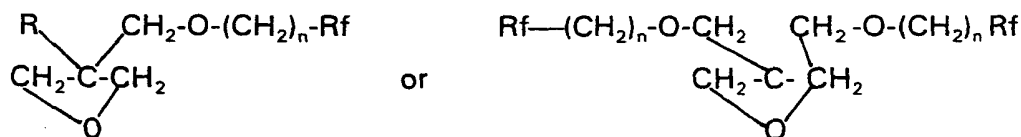
Polyfluorooxetane oligomers and polymers can be functional-
5 ized with acrylate, or methacrylate, or allylic, end groups and thereafter
used as a polyacrylate, or methacrylate, or allylic, in a radiation curable
coating composition. These polyfluorooxetanes could also be called
fluorinated polyoxetanes or polyoxetanes with partially fluorinated pen-
dant side groups (chains). These pendant side groups include the Rf
10 groups defined later. The coating composition comprises the traditional
components to a radiation curable coating which include the acrylate, or
methacrylate, or allylic, terminated oligomers or polymers, monomer, op-
tionally UV initiator, optionally a second polyfunctional acrylate, or meth-
acrylate, or allylic, oligomer or polymer or a polyester, and optionally other
15 additives like pigments, plasticizers, rheology modifiers etc. While the ac-
rylate, or methacrylate, or allylic, terminated polyfluorooxetane can be
used in about any concentration in the radiation curable coating it is gen-
erally effective in an amount of repeating units of the illustrated formula
from about 0.005, or from about 0.1, or from about 1 to about 10 weight
20 percent based on the weight of the coating composition.

In a cationic UV system the oxirane ring is opened by a nucleo-
phile. In a UV or e-beam initiated system the acrylate, or methacrylate, or
allylic, functional end from a urethane reaction (isocyanate), an epoxy ac-
rylate, transesterification or even an epichlorhydrin reaction, are polymer-
25 ized, i.e., cured. The functionalized polyfluorooxetane can be produced by
several methods, but due to the lower reactivity of the hydroxyl groups of
the polyfluorooxetane with isocyanate and epoxy groups, it is desirable to
sequentially add to reactants so nearly complete functionalization of the
polyfluorooxetane can be achieved. Typically an isocyanate or epoxy
30 functionalize polyfluorooxetane is first formed and that is reacted with a
hydroxy alkyl acrylate, or methacrylate, or allylic, to form the urethane ac-

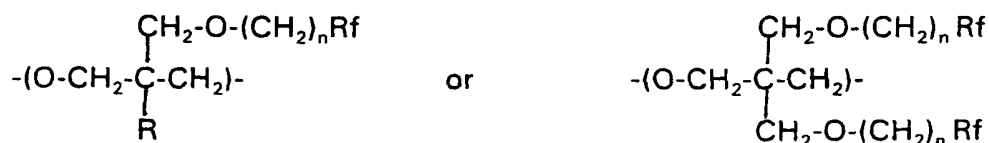
rylate, or methacrylate, or allylic, or epoxy acrylate, or methacrylate, or allylic, terminated polyfluorooxetane. Alternatively the acrylate, or methacrylate, or allylic, can be epoxy or isocyanate functionalized and that compound reacted with the polyfluorooxetane.

5 The polyfluorooxetane when incorporated into a coating via the acrylate group provides improved wear resistance, scratch resistance, mar resistance, stain resistance, leveling, improved slip and lower coefficient of friction. There are generally enhanced surface properties relative to a coating without the additive. While not being bound by any explanation, it is anticipated that the polyfluorooxetane, to the extent possible while
10 blended with the other components and after curing, migrates to the interfaces between the coating and the substrate and the interface between the coating and the atmosphere providing increased wetting at the solid interface improving adhesion, wetting, gloss/appearance and leveling,
15 lower surface tension at the atmosphere interface for improve wear and stain resistance at the atmosphere interface. The application is focused on coating because molded articles and thicker compositions are more difficult to cure with radiation cures, but this does not preclude their use in thick articles.

20 The oxetane monomer used to form the polyfluorooxetane has the structure



and the repeating unit derived from the oxetane monomer has the formula



where each n is the same or different and independently, is an integer between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms, and each R_f is the same or different and individually on each repeat unit is a linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or each R_f is the same or different and individually is an oxaperfluorinated polyether having from 4 to 60 carbon atoms

Another focus of this application is adding the properties of the partially of fully fluorinated pendant groups without detracting from the inherent physical properties typically found in vinyl ester resin compositions. This can be achieved as the polyoxetane backbone is very similar in polarity and molecular flexibility to the polyethers (e.g. ethylene oxide and propylene oxide) used in many vinyl ester resin compositions. Further the polyoxetane in being available as a polyol can be conveniently reacted in the network via epoxy or isocyanate reactive groups which are common to vinyl ester resin compositions.

The substrates for the radiation curable coating include thermoplastic or thermoset plastics, paper, metals, wovens and nonwovens, cellulosics other than paper, etc. Preferred plastics include polyvinyl chloride, polyesters, polycarbonates. The plastics may be formed into furniture, cabinets, flooring overlay, building products, etc. Preferred cellulosics include wood products such as furniture, cabinets, wood flooring, paper, and the like. The coating is useful as a protective coating for any of the above substrates.

The coating can be modified to be flexible or rigid depending on the flexibility of the substrate. The polarity of the coating can be adjusted by changing the polarity of the acrylate, or methacrylate, or allylic, terminated components or the monomer to make it compatible with the substrate. The coating can be made more flexible by using less

crosslinking polyfunctional acrylate, or methacrylate, or allylic, or choosing a monomer that forms a lower glass transition temperature polymer. The backbone of the polyfunctional acrylate, or methacrylate, or allylic, can also be chosen to result in a softer lower flexural modulus coating.

5 Various curing options are available for the coating composition. As shown in the examples some of the components cure upon standing if polymerization inhibitors are not present. Electron beam irradiation can be used to cure the coatings. If ultraviolet (UV) activated free radical initiators are present, ultraviolet light can activate curing. Combinations of
10 two curatives from a single type can be used. The amount and types of curatives are well known to the art of radiation and UV curatives. The amount of curatives will be set forth as an effective amount that converts at least 50, 75 or 90 or even 100 weight percent of the polymerizable components of the coating into nonextractable gel.

15 The monomers that can be used in the coating are generally any unsaturated monomers copolymerizable through said unsaturation with the acrylate, or methacrylate, or allylic, functionalized polyfluorooxetane.

Monomers can be distinguished from the latter described polyfunctional oligomers or acrylate, or methacrylate, or allylic, functionalized polyfunctional oligomers by the fact that monomers are generally polyfunctional
20 while polyfunctional reactants form crosslinked polymers. Further monomers are generally lower in viscosity and more volatile than the oligomers. Preferred monomers include vinyl aromatic monomers of 8 to 12 carbon atoms, acrylates of 4 to 30 carbon atoms, and N-vinyl pyrrolidone. The monomer(s) are generally selected based upon a variety of
25 considerations including volatility, relative health hazards from exposure, their reactivity ratios in copolymerization with the acrylate terminated polymers and oligomers, etc. It is generally desirable that at least 50, 70, or 80 mole percent of the oligomers are copolymerized into monomers and other reactants before 90 mole percent of the monomer is
30 converted to polymer.

The polyfunctional oligomers and polymers (other than the acrylate, or methacrylate, or allylic, terminated polyfluorooxetane) are conventional components in radiation curable coatings. They are characterized by the presence of two or more unsaturated carbon to carbon double bonds that can copolymerize with the monomer(s), or oxirane terminated (co)polymer (cationic). These components are added in effective amounts to change the physical properties of the coatings such as crosslink density, which has an effect on modulus and strength. These reactants contribute significantly to the solvent resistance of the cured coatings as the crosslinks they provide inhibit swelling in common solvents. Examples of these components include Ebycyl 4833, an acrylated aliphatic urethane oligomer; TRPGDA, tripropylene glycol diacrylate; and TMPTA, trimethylolpropane triacrylate.

Ultraviolet light (UV) activated curative(s) may be used in the coating in an effective amount to cause polymerization of the monomer(s) and crosslinking by the polyfunctional oligomers and polymers. These curatives may be any chemical compound that can generate free radicals on exposure to ultraviolet radiation. UV activated curatives are set forth in US 5,411,996; 4,882,201 and 4,279,717 herein incorporated by reference. Other UV activated curatives such as Cyacure UVR-6110 and Cyacure UVI-6974 used in the examples are commercially available and known to the art.

Other components to the coating include fillers such as TiO_2 , and other pigments and colorants; antigloss agents such as precipitated silicas; dyes; plasticizers such as ester oils, triglycerides, hydrocarbon oils, waxes; flow modifiers such as rheology modifiers, shear thinning agents; accelerators such as amines; and wetting agents and surface modifiers for fillers.

The oxetane polymer (including copolymers, terpolymers, etc.) generally have one or more and preferably two or more terminal hydroxyl groups. Molecules with one or more hydroxyl groups are gener-

ally referred to as polyols. These desirably have degrees of polymeriza-
tion from about 2, 3, or 4 to about 150, more desirably from about 3 to
about 100 and preferably from about 3 to about 30 or 50. Desirably
they have from about 1.5 to about 3.2 hydroxyl groups per molecule on
average.

The reactivity of the polyfluorooxetane with isocyanate groups
and with epoxy groups is generally not as good as the reactivity of con-
ventional polyethers such as poly(ethylene oxide) with isocyanates and
epoxies. Therefore it is desirable to control the reaction sequence and
reaction ratios to maximize the functionalization of the polyfluorooxetane
with the isocyanate or epoxy groups and then with the acrylate func-
tionality.

One procedure is to first react the polyfluorooxetane with the di or
poly isocyanate or di or poly epoxy compound to generate (form) isocya-
nate or epoxy groups on the ends (termini) of the polyfluorooxetane (iso-
cyanate or epoxy terminated polyfluorooxetane). Catalysts and or other
favorable reaction conditions (heating) may be employed to force these
reactions towards completion.

The reaction between the hydroxy groups and the isocyanate or
epoxy groups can be monitored by various chemical analysis methods to
optimize reaction conditions. Desirably at least 2 moles of isocyanate
groups or epoxy groups are present for every mole of hydroxyl groups.
This promotes end capping of the polyfluorooxetane rather than chain
extension, which is the predominant reaction when the ratio of isocya-
nate or epoxy groups to hydroxyl groups is 1:1. In most embodiments
chain extension is not desirable as the resulting higher molecular weight
polymers increase the coating viscosity and may decrease the number of
load bearing chains, which can decrease physical properties. Desirably
the moles of isocyanate groups or epoxy groups is between 2 and 3 per
mole of hydroxyl groups and more desirably between 2.0 and 2.5. Other
reaction conditions can be optimized to further limit chain extension.

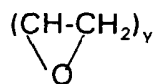
After an isocyanate or epoxy terminated polyfluorooxetane is formed it can be reacted with an acrylate, or methacrylate, or allylic, molecule that has a pendant group which is reactive with an isocyanate or epoxy group to form a chemical bond between the isocyanate group or epoxy group and the acrylate, or methacrylate, or allylic. Hydroxy alkyl acrylates, such as hydroxy ethyl acrylate or hydroxy ethyl (alk)acrylate are preferred as the hydroxyl groups forms a very chemically stable urethane linkage. The use of "(alk)" before acrylate is used to indicate the optional inclusion of alkyl substituents of 1 to 6 carbon atoms. Other acrylate functional monomer(s) that can be attached to the isocyanate or epoxy functionalized polyfluorooxetane include amine functional acrylates, acrylamides, or acrylic acids.

Another way to achieve the same result is to react the di or polyfunctional isocyanate or epoxy compound with the acrylate, or methacrylate, or allylic, functional monomer in a mole ratio of isocyanate or epoxy groups to the functional group of the acrylate, or methacrylate, or allylic, (e.g. hydroxyl) of above 2:1, more desirably from about 2 to 3 and preferably from about 2 to about 2.5. This will form an isocyanate or epoxy functionalized acrylate, or methacrylate, or allylic, under the right conditions. These isocyanate or epoxy functional acrylates, or methacrylate, or allylic, can be reacted with the polyfluorooxetane to produce an acrylate, or methacrylate, or allylic, terminated polyfluorooxetane.

The di or polyisocyanate compound can generally be any compound of the formula $X-(NCO)_y$, where y is an integer above 2 and X is an aliphatic group of 4 to 100 carbon atoms, an aromatic group of 6 to 20 carbon atoms, or a combination of alkyl and aromatic groups or alkyl substituted aromatic or aromatic substituted alkyl of 7 to 30 carbon atoms or oligomers thereof. These isocyanate compounds are well known to the art. Preferred ones are 4',4-methylene diphenyl isocyanate (MDI)

as well as polymeric MDI, which is a liquid rather than a crystalline solid, toluene diisocyanate, 1,6-hexane diisocyanate, isophorone (preferred) diisocyanate, trimethylhexane diisocyanate, etc.

Similarly the epoxy compounds can generally have the formula Z-



where y is as previously defined and Z is a di or polyvalent group having from 2 to 100 carbon atoms, often 1 or more oxygen atoms, and sometimes other heteroatoms besides oxygen and hydrogen. It is desirable to keep the molecular weight of the epoxy compound as low as higher molecular weights will increase the viscosity.

Experimental

EXAMPLES 1-5

Poly-fluorinated oxetane diols (poly-FOX) were prepared using the method described in U.S. Patent 5,650,483 using a BF_3 -THF initiating species to produce an oxetane-tetrahydrofuran copolymer with the specified level of tetrahydrofuran comonomer.

Example	Rf	Description	Amount of THF in polymer (mole %)	Number average molecular weight
1	CF_3	Poly-3-FOX	6.4	2800
2	CF_3	Poly-3-FOX	6.2	3400
3	CF_3	Poly-3-FOX	8.2	2300
4	CF_3	Poly-3-FOX	26.4	4200
5	$-(\text{CF}_2)_2-\text{CF}_3$	Poly-7-FOX	7.3	2200

EXAMPLE 6

Preparation of Di-urethane-acrylate of Poly-7-FOX

A 250 mL, 3 neck round bottom flask fitted with a mechanical stirrer and a thermometer was dried under nitrogen and charged with poly-7-FOX diol (polyfluorooxetane diol with heptafluoro group) (24.3 grams, 9.1 meq.) from Example 5. Isophorone diisocyanate (3.0 grams, 27.2

meq) and dibutyl tin dilaurate (12 mg) were added and the mixture was heated at 70 C for 14 hours. The reaction mixture was cooled to room temperature and washed with heptane (2 times 100 mL each). The isocyanate-terminated poly-7-FOX prepolymer was then dissolved in tetrahydrofuran (50 mL) and treated with dibutyltin dilaurate (12 mg). The resulting solution was reacted with 2-hydroxyethylacrylate (HEA, 1.16 gram, 10 meq) at room temperature. No observable exotherm was observed on the addition of HEA. The progress of the reaction was monitored by following the disappearance of the isocyanate band in an infrared spectroscopic spectrum (IR) at 2270 cm^{-1} . The mixture was heated at a temperature of 60 C for 4 hours. On completion, as indicated by the disappearance of the NCO band in the IR, the reaction mixture was precipitated into water (450 mL). The resulting solution was dried over magnesium sulfate, filtered and stripped of solvent under reduced pressure to produce 17.2 grams of a urethane-acrylate terminated poly-7-FOX.

EXAMPLES 7-10

The following general procedure was used to generate examples 7-10. A 3-liter, 4-neck round bottom flask fitted with a mechanical stirrer, condenser, and a thermometer was dried under nitrogen and charged with poly-3-FOX diol (405 grams, 0.29 eq). Isophorone diisocyanate (69 grams, 0.61 eq) and dibutyltin dilaurate (0.2 gram) were added at room temperature. A mild exotherm resulting in a temperature increase from 26 to 30 C was observed. The resulting mixture was stirred at ambient temperature for one hour and then heated to 65 C for one hour. The mixture was then cooled to 30 C and 2-hydroxyethyl acrylate (37.4 grams, 0.32 eq.) was added over a thirty-minute period. The mixture was stirred at ambient temperature for 16 hours at which point IR analysis revealed the presence of a strong NCO stretching band at 2270 cm^{-1} . Dibutyltin dilaurate catalyst (0.3 grams) was added and the mixture was heated at 60 C for 3 hours and then at ambient temperature for 16

hours. A 50 gram sample of acrylate material was removed. An inhibitor (4-methoxyphenol, 0.47 grams) was added and the mixture was stirred vigorously to disperse the inhibitor. The resulting mixture, a colorless viscous oil, was transferred to disperse the inhibitor. The resulting mixture, a colorless viscous oil, was transferred to a plastic carboy and retained for further use. Overall 505 grams of the co-polymer was isolated representing a yield of 98.7%.

Acrylated Example	Starting poly-FOX Diol
7	1
8	2
9	3
10	4

Testing Procedures for UV Coatings

Burnish	The mar resistance was evaluated by putting a pestle onto the coated paper and making a circular motion with firm pressure. If a burnish mar resulted, it would generally not be removed through rubbing with isopropyl alcohol.
Adhesion	Cross-Hatch
Hoffman Scratch Test	Gardner Scratch, Adhesion and Mar Tester
60 Gloss %	The gloss of a coating was measured with the Gardner gloss meter set at a 60 degree angle of incidence. Two separate measurements of five readings were taken.
Contact Angle	The contact angles were measured with water as the liquid using the First Ten Angstrom FTA 200. Three contact angles were measured at different locations on each specimen. During the data collection process, the computer recorded an image of the drop every 0.1 seconds for 15 seconds (150 images), and calculates a contact angle for each image.

General Procedure for Preparation of Coating Formulations:

The monomers and acrylated resins (e.g. Ebecryl 81, Ebecryl 4833, TRPGDA, and TMPTA) were weighted into a reactor and mixed at 50 C for 30 minutes. The reactor was cooled to room temperature (approximately 25 C) while mixing. To the reactor contents were added the acrylated-poly-FOX prepolymer or the FOX/ZOX monomer, and any of the constituents of the formulation (i.e. deglossing agent (silica), coalescent (N-vinyl pyrrolidone), initiator (not needed in electron beam cures) (Irgacure 500), antioxidant (Irganox 1035)) and the system was stirred until completely mixed (approximately 30 minutes).

General Procedure for UV Curing of Coatings:

Coating formulations were applied to the substrates via gravure cylinder or wire wound rods at a nominal thickness of 1 to 2 mil. The coated substrates were placed on a conveyor at a speed of approximately 20 feet/min through the curing chamber. The mercury lamp emitted a 0.045 J/sq cm dose and a 0.055 W/sq cm intensity in the UVC region as measured by the EIT Powerpuck.

General Formulation for UV Coatings for Application to PVC Substrates

Chemical	Tradename or Abbreviation	Weight Percent
Acrylated aliphatic urethane oligomer	Ebecryl 4833	36.36 minus level of FOX diacrylate
Tripropylene glycol diacrylate	TRPGDA	20.65
Trimethylolpropane triacrylate	TMPTA	5.20
Benzophenone and 1-hydroxy acetophenone	Irgacure 500	6.61
N-methylethanolamine		1.76
Antioxidant	Irganox 1035	0.29
N-vinylpyrrolidone	NVP	8.47
Low viscosity amine modified acrylated polyester oligomer	Ebecryl 81	20.66
Diacrylated Poly-3-FOX		variable

The aliphatic urethane was warmed to 110 to 130 F and blended to the polyol-polyether, TMPTA, TMPDA, NVP and di-urethane acrylate poly-3-FOX at 106 C for 30 minutes. The formulations were allowed to cool before introduction of photo-initiators (i.e. benzophenone), 2-hydroxyl-2-methyl phenyl propane, and the antioxidant.

The formulations were applied to the flexible black PVC with RDS 05 wire wound rod at ambient temperature, and cured on a Union Carbide Linde PDCS UV unit with the following setup:

1. One 200 watt/inch lamp was on
2. Line speed of approximately 30 feet per minute
3. Samples were taped on the topside to the conveyor belt and sent through one at a time.

EXAMPLE 11

Properties of UV Coatings Effect of Level of Acrylated Poly-3-FOX on Coating Performance when Applied to Flexible PVC Cured Under Air

Example 7 Wt. %	Gloss %	Hoffman Scratch Resis- tance (g)	Mar Resistance
0.0	51	1200	8
0.5	91	2000	10
1.0	96	2000	10
2.0	93	2300	10
4.0	97	2300	10

EXAMPLES 12 TO 16

Properties of UV Coatings, Effect of FOX Copolymer Composition on
Coating Performance when Applied to Flexible PVC Cured Under Nitro-
gen

Example	Poly-3-FOX diacrylate used in Example	Weight Percent of Poly-3-FOX diacrylate	Hoffman Scratch (g)	Coefficient of Friction		Cracking
				static	kinetic	
12	Control	0	1900	3.48	3.61	Severe
13	7	3	2900	1.67	0.50	Severe
14	8	3	2900	0.89	2.23	Severe
15	9	3	2900	1.24	1.60	Moderate
16	10	3	2900	3.51	4.40	Severe

EXAMPLE 17**Formulation of Paper Coatings Cured via UV Radiation**

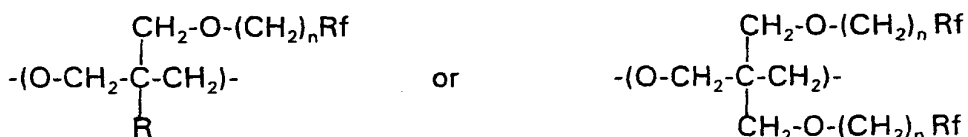
Ingredient	Amount Weight %
Ebecryl 4833	9.96
Ebecryl 81	19.54
Trimethylol propane triacrylate	20.87
Tripropylene glycol diacrylate	26.13
Ebecryl 8301	6.26
Irgacure 500	3.13
N-Methyl diethanol amine	1.84
Poly-3-FOX Acrylate	0.80
Syloid 308	3.57
Polyfluo 523XF	4.24
Polyfluo 717XF	1.69
Property	Value
Hoffmann Scratch	500 g
Mar Resistance	8
Cross-Hatch Adhesion	100%

5

While in accordance with the patent statutes the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

WHAT IS CLAIMED IS:

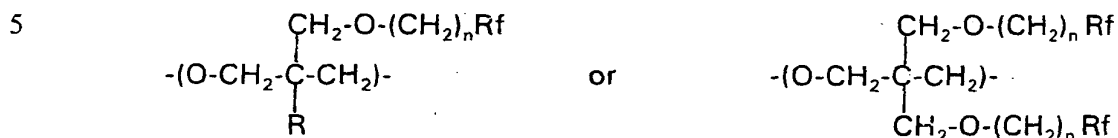
1. An acrylate, or methacrylate, or allylic, terminated polymer
 5 (oligomer) which is copolymerizable with styrene, methyl methacrylate or
 N-vinyl pyrrolidone, said polymer comprising the reaction product of a) at
 least one polyol, b) at least one di or polyisocyanate, and c) at least one
 hydroxy alkyl acrylate, or methacrylate, or allylic, wherein either i) a and b
 are reacted to form an isocyanate terminated oligomer or polymer and said
 10 isocyanate terminated oligomer or polymer is reacted with c to form an ac-
 rylate, or methacrylate, or allylic, terminated oligomer or polymer or ii) b is
 reacted with c to form an isocyanate functionalized acrylate, or methacryl-
 ate, or allylic, which is then reacted with a to form an acrylate, or methac-
 rylate, or allylic, terminated oligomer or polymer, where said at least one
 15 polyol comprises at least 10 weight percent repeating units of the formula



- 20 where each n is the same or different and independently, is an integer
 between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms, and
 each Rf is the same or different and individually on each repeat unit is a
 linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum
 25 of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms
 and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or
 each Rf is the same or different and individually is an oxaperfluorinated
 polyether having from 4 to 60 carbon atoms

30

2. A polymer according to claim 1, wherein said polyol is a co-polymer of at least an oxetane with a pendant fluorinated alkyl according to the formula



where R is a hydrogen and Rf is an alkyl of 1 to 15 carbon atoms.

3. A polymer or oligomer according to claim 2, wherein said polyol includes repeating units resulting from the ring opening polymerization of tetrahydrofuran and derivatives thereof.

4. A polymer or oligomer according to claim 2, wherein said polyol has a degree of polymerization from about 3 to about 150.

5. A polymer or oligomer according to claim 2, wherein said polyol comprises a diol and is reacted with at least two moles of a diisocyanate to form a polyol with two terminal isocyanate groups.

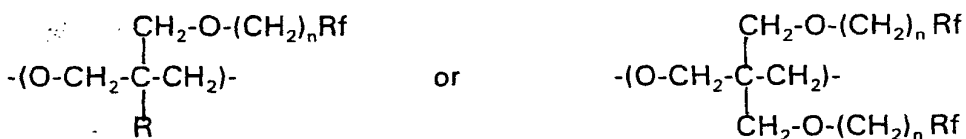
6. A polymer or oligomer according to claim 2, wherein said polyol has a degree of polymerization from about 3 to about 50.

7. A polymer or oligomer according to claim 2, wherein said polyol has a degree of polymerization from about 3 to about 30.

8. A process for forming a partially fluorinated acrylate, or methacrylate, or allylic, terminated oligomer comprising reacting a partially fluorinated polyoxetane containing polyol, optionally including non-oxetane repeating units either a) sequentially with a di or polyisocyanate forming

an isocyanate terminated oligomer or polymer and then reacting that isocyanate terminated oligomer or polymer with a hydroxyl containing acrylate, or methacrylate, or allylic, and forming an acrylate, or methacrylate, or allylic, terminated polyoxetane oligomer or polymer or b) in a single step with an isocyanate functionalized acrylate, or methacrylate, or allylic, forming an acrylate, or methacrylate, or allylic, terminated polyoxetane oligomer or polymer.

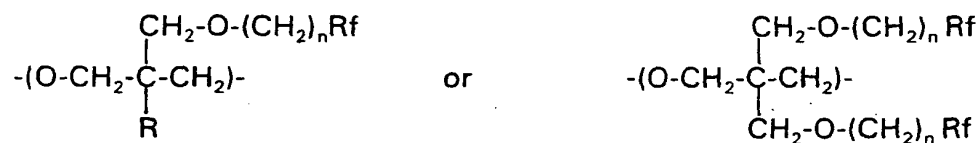
9. A process according to claim 8 wherein the polyoxetane containing polyol comprises repeating units of the formula



where each n is the same or different and independently, is an integer between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms, and each Rf is the same or different and individually on each repeat unit is a linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or each Rf is the same or different and individually is an oxaperfluorinated polyether having from 4 to 60 carbon atoms

10. A process according to claim 8, wherein said polyoxetane containing polyol is a difunctional polyol and is reacted with at least two moles of a diisocyanate forming said isocyanate terminated polyoxetane oligomer or polymer which is then reacted with said hydroxy containing alkyl acrylate, or methacrylate, or allylic.

11. An acrylate, or methacrylate, or allylic, terminated polymer which is copolymerizable with styrene, methyl methacrylate or N-vinyl pyrrolidone, said polymer comprising the reaction product of a) at least one polyol, b) at least one di or polyepoxy compound, and c) at least one hydroxy alkyl acrylate, or methacrylate, or allylic, wherein either i) a and b are reacted to form an epoxy terminated oligomer or polymer and said epoxy terminated oligomer or polymer is reacted with c to form an acrylate, or methacrylate, or allylic, terminated oligomer or polymer or ii) b is reacted with c to form an epoxy functionalized acrylate, or methacrylate, or allylic, which is then reacted with a to form a acrylate, or methacrylate, or allylic, terminated oligomer or polymer, where said at least one polyol comprises at least 10 weight percent repeating units of the formula

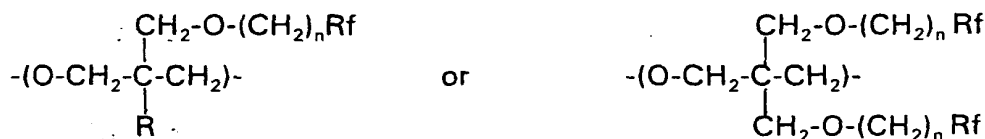


where each n is the same or different and independently, is an integer between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms; and each Rf is the same or different and individually on each repeat unit is a linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or each Rf is the same or different and individually is an oxaperfluorinated polyether having from 4 to 60 carbon atoms

12. A process for forming a partially fluorinated acrylate, or methacrylate, or allylic, terminated oligomer comprising reacting a partially fluorinated polyoxetane containing polyol, optionally including non-oxetane repeating units either a) sequentially with a di or polyepoxy compound forming an epoxy terminated oligomer or polymer and then reacting that

epoxy terminated oligomer or polymer with a hydroxyl containing acrylate, or methacrylate, or allylic, forming an acrylate, or methacrylate, or allylic, terminated polyoxetain oligomer or polymer or b) in a single step with an epoxy functionalized acrylate, or methacrylate, or allylic, forming an acrylate, or methacrylate, or allylic, terminated polyoxetane oligomer or polymer.

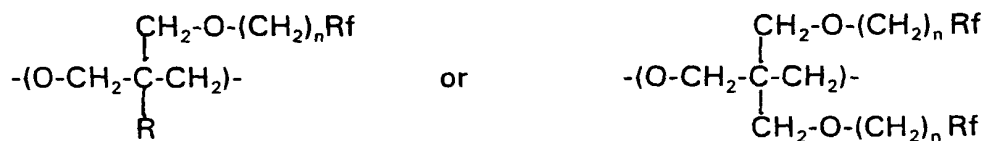
13. A process according to claim 12, wherein the polyoxetane containing polyol comprises repeating units of the formula



where each n is the same or different and independently, is an integer between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms, and each Rf is the same or different and individually on each repeat unit is a linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or each Rf is the same or different and individually is an oxaperfluorinated polyether having from 4 to 60 carbon atoms

14. A coating composition comprising;

a) an acrylate, or methacrylate, or allylic, terminated oligomer or polymer with at least 10 weight percent of repeating units having the formula



where each n is the same or different and independently, is an integer between 1 and 5, R is hydrogen or an alkyl of 1 to 6 carbon atoms, and each R_f is the same or different and individually on each repeat unit is a linear or branched fluorinated alkyl of 1 to 20 carbon atoms, a minimum of 75 percent of the non-carbon atoms of the alkyl being fluorine atoms and optionally the remaining non-carbon atoms being H, I, Cl, or Br; or each R_f is the same or different and individually is an oxaperfluorinated polyether having from 4 to 60 carbon atoms

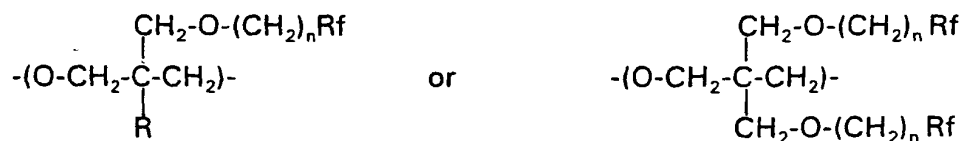
b) at least one monomer copolymerizable with said acrylate, or methacrylate, or allylic, terminated oligomer, and

c) optionally a free radical initiator which is activated by ultraviolet radiation, and

d) optionally a polyfunctional acrylate, or methacrylate, or allylic, monomer, or oligomer.

15. A coating composition according to claim 14, wherein said acrylate, or methacrylate, or allylic, terminated oligomer or polymer is derived from a polyoxetane polyol, optionally including non-oxetane repeating units, having a degree of polymerization from about 3 to about 150 coupled to the acrylate, or methacrylate, or allylic, terminal groups via reactions using a diepoxy or diisocyanate compound.

16. A coating composition according to claim 15, wherein said repeating units of the formula

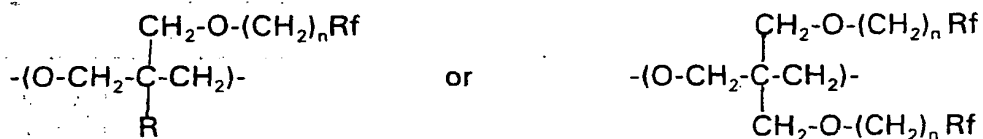


comprise from about 1 to about 20 weight percent of said coating composition.

17. A coating composition according to claim 14, wherein Rf is a linear or branched fluorinated alkyl of from about 1 to about 15 carbon atoms.

5 18. A coating composition according to claim 14, which has been cured by electron beam irradiation.

10 19. A coating composition according to claim 14, wherein said acrylate, or methacrylate, or allylic, terminated oligomer or polymer is derived from a copolymer of said oxetane of the formula



15 and tetrahydrofuran.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/13998

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/50 C08G18/67 C09D175/16 C09D163/10 C08F290/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 23828 A (DSM NV) 8 August 1996 (1996-08-08) page 2, line 35 -page 5, line 35 examples 1,4	1,8,10, 14,15,18
A	US 4 051 195 A (MCWHORTER WAYNE F) 27 September 1977 (1977-09-27) column 1, line 52 -column 4, line 24 example 3	11,12,15
A	US 5 043 221 A (KOLESKE JOSEPH V) 27 August 1991 (1991-08-27) column 2, line 13 - line 36 column 7, line 9 -column 8, line 68; table I	12,15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

12 September 2000

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INTERNATIONAL SEARCH REPORT

In ☐ International Application No

PCT/US 00/13998

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 674 951 A (LIVIGNI RUSSELL A ET AL) 7 October 1997 (1997-10-07) cited in the application column 1, line 39 -column 4, line 24 column 13, line 25 -column 14, line 67</p>	1-5,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/13998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W0 9623828 A	08-08-1996	AU 1467995 A EP 0807136 A JP 11503768 T	21-08-1996 19-11-1997 30-03-1999
US 4051195 A	27-09-1977	NONE	
US 5043221 A	27-08-1991	CA 1312040 A DE 3686941 A DE 3686941 T EP 0233358 A JP 1801217 C JP 5008948 B JP 62230861 A KR 9202780 B MX 174472 B US 5155143 A ZA 8609519 A	29-12-1992 12-11-1992 18-02-1993 26-08-1987 12-11-1993 03-02-1993 09-10-1987 03-04-1992 18-05-1994 13-10-1992 26-08-1987
US 5674951 A	07-10-1997	NONE	

